Top-Seeded Melt-Growth of $YBa_2Cu_3O_x$ Crystals for Neutron Diffraction Studies

D. C. Peets,[1,*] Ruixing Liang,[1,†] C. Stock,[2] W. J. L. Buyers,[3,†] Z. Tun,[3]
L. Taillefer,[2,†] R. J. Birgeneau,[2,†] D. A. Bonn,[1,†] and W. N. Hardy[1,†]

[1]*Department of Physics and Astronomy, University of British Columbia, Vancouver, BC, Canada*
[2]*Physics Department, University of Toronto, Toronto, ON, Canada*
[3]*National Research Council, Chalk River, ON, Canada*

(Dated: February 1, 2008)

We have grown cubic centimetre-size crystals of $YBa_2Cu_3O_x$ suitable for neutron studies, by a top-seeded melt-growth technique. Growth conditions were optimized with an eye toward maximizing phase purity. It was found that the addition of 2% Y_2BaCuO_5 and 0.5% Pt (by mass) were required to prevent melt loss and to obtain the highest crystallinity. A neutron diffraction study on a mosaic of six such crystals found that the final Y_2BaCuO_5 concentration was 5%, while other impurity phases comprised less than 1% by volume. The oxygen content was set to $x = 6.5$, the crystals were detwinned and then carefully annealed to give the well-ordered ortho-II phase. The neutron study determined that 70% of the mosaic's volume was in the majority orthorhomic domain. The neutron (0 0 6) and (1 1 0) rocking curve widths were $\sim 1^\circ$ per crystal and $\sim 2.2^\circ$ for the mosaic, and the oxygen chain correlation lengths were >100 Å in the *a*- and *b*-directions and ~50 Å in the *c*-direction.

Keywords: crystal growth, top-seeded melt-growth, Ortho-II, YBCO, neutron scattering

1. MOTIVATION

Neutron scattering is an extremely powerful technique for investigating spin fluctuation and magnetic ordering in superconducting samples. However, to obtain reasonable signal to noise one requires sample sizes on the order of several cubic centimetres. The self-flux technique[1, 2], which produces the highest-quality $YBa_2Cu_3O_x$ single crystals and is the primary method for growing crystals for fundamental research, has thus far only been able to yield crystals as large as 5 mm×5 mm×$\frac{1}{2}$ mm. Additionally, $YBa_2Cu_3O_x$ is difficult to grow in an image furnace, due primarily to the low solubility of Y_2BaCuO_5 in the BaO-CuO melt[3].

The top-seeded melt-growth technique has been widely used to grow $YBa_2Cu_3O_x$ crystals as large as several inches[4, 5, 6, 7, 8, 9, 10, 11], but these crystals were intended for applications such as magnetic levitation. The growth conditions were therefore optimized for maximal critical current densities, a criterion which requires defects for flux pinning. As a result, the crystals typically contained 10-30% Y_2BaCuO_5 and $\frac{1}{2}$-1% Pt by mass, and were not well suited to neutron studies since the scattering from the inclusions can overlap the scattering from the $YBa_2Cu_3O_x$.

This study aimed to optimize the top-seeded melt-growth technique for the lowest concentration of impurity phase inclusions and best crystallinity (minimum mosaic spread). The resulting cubic centimetre-size $YBa_2Cu_3O_x$ crystals were then annealed to the oxygen-ordered ortho-II phase ($x = 6.5$). This allows a neutron scattering study on spin fluctuations and magnetic ordering to be carried out on higher-purity, well-ordered crystals.

2. CRYSTAL GROWTH

Precursor $YBa_2Cu_3O_x$ and Y_2BaCuO_5 powders were made by preparing stoichiometric mixtures of Y_2O_3 (99.999% pure), $BaCO_3$ (99.999%) and CuO (99.995%), then calcining in $BaZrO_3$ crucibles at ~950°C until the reaction was complete as determined by X-ray diffraction. The $YBa_2Cu_3O_x$, Y_2BaCuO_5 and Pt powders were mixed in an agate mortar under ethanol, then pressed in a cylindrical mold under 300 MPa of hydrostatic pressure. The resulting pellet was approximately 13 mm high by 12 mm in diameter, and had a mass of ~10 g.

The addition of a small amount of Pt[12] is required to prevent melt loss during growth by increasing the melt's viscosity. We found that $\frac{1}{2}$% Pt by mass was required for this purpose. Without the addition of Y_2BaCuO_5, the crystals were porous, had poor mosaic spread, and contained BaO-CuO flux inclusions. Best results were obtained when the pellet contained 2% Y_2BaCuO_5 by mass.

A higher concentration of Y_2BaCuO_5 was found to be necessary for proper seeding, so a small quantity of Y_2BaCuO_5-rich powder (10% Y_2BaCuO_5 by mass) was added to the top of the pellet prior to pressing. This layer constituted ~0.4% of the pellet.

$NdBa_2Cu_3O_x$ was chosen as a seed crystal for its near-perfect lattice match and for having a melting temperature ~80°C higher than that of $YBa_2Cu_3O_x$. The seed and pellet were placed on a disc-shaped substrate, loaded into a three-zone vertical tube furnace, and subjected to the temperature program shown in figure 1. After a sintering step at 990°C, a temperature gradient of $\sim 5\frac{^\circ\mathrm{C}}{\mathrm{cm}}$ was applied and the pellet was melted, then slowly cooled. This effectively moved the peritectic temperature

*Electronic address: dpeets@physics.ubc.ca
†Canadian Institute for Advanced Research

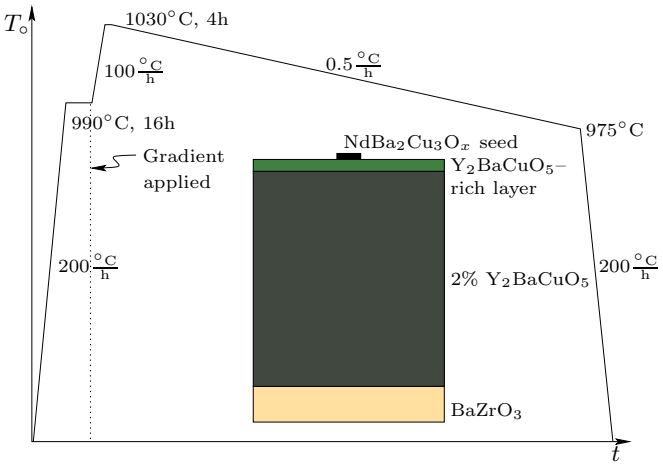

FIG. 1: The crystallization furnace program, where $T_\circ$ is the average temperature of the pellet and t is the time. The inset depicts the growth setup, showing the geometry of the pellet, seed and substrate.

through the pellet, from seed to substrate, over the course of several days.

While several substrates were tested, including alumina (Al_2O_3) and single-crystalline MgO and $SrTiO_3$, satisfactory results were only obtained using $BaZrO_3$ discs.

The top of each crystal had an elevated Y_2BaCuO_5 concentration and often extraneous domains near the edge, while the bottom had a layer with a high concentration of impurity phases which had been pushed there by the growth front (including much of the platinum). The top and bottom millimetres of the crystal were accordingly cut off using a diamond saw. Additionally, a millimetre was removed from two opposite sides, to create flat (1 0 0)/(0 1 0) faces for detwinning. We were able to align the crystals visually to within a degree.

To form the oxygen-ordered ortho-II phase of $YBa_2Cu_3O_{6.5}$, which has alternating full and empty chains, the oxygen content was set to $x = 6.53$ by annealing for one week in 1 atm oxygen gas, at 760.0°C, in the same conditions as for single crystals[13]. It has been reported that the ortho-II phase's longest oxygen correlation lengths may be realized at oxygen contents slightly above 6.50[14].

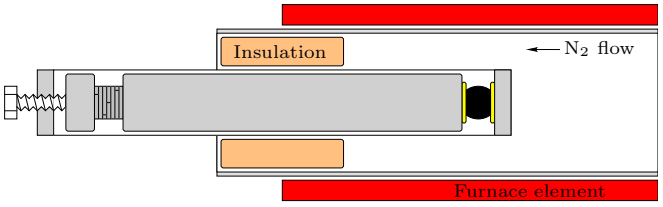

FIG. 2: Schematic diagram of the detwinner.

A specialized detwinner, depicted schematically in figure 2, was built for these crystals. The sample was loaded into it, sandwiched between two gold pads to ensure that the pressure was uniformly distributed on the two a-axis faces. A uniaxial pressure of ∼150 MPa (1500 atm) was applied, as gauged by monitoring the compression of several lock washers with known spring constants. The detwinner was loaded into a horizontal tube furnace and heated to 350°C in flowing nitrogen for 30 minutes, then cooled to room temperature at 60°C per hour. The crystal's mass was not observed to be changed by this process, indicating no measurable change in the crystal's oxygen content during detwinning.

Once detwinned, the crystals were annealed at 60°C in sealed containers for two weeks to establish ortho-II oxygen ordering.

3. ANALYSIS

Magnetization measurements in a Quantum Design SQUID magnetometer found the crystals' T_c to be 59 K, and 2.5 K wide (field-cooled, $H = 1.5$ Oe, $\vec{H} \parallel \vec{c}$).

A sample was subjected to EDX compositional analysis to determine the shape and distribution of impurity phases. Y_2BaCuO_5 was only observed at the base of the pellet, near the growth front, but the equipment's $\sim 1\mu$m resolution makes it insensitive to small inclusions in the bulk. Two Pt-containing phases were found, one of which was consistent with the formula $Y_2PtBa_3Cu_2O_{10}$. Neutron scans found weak impurity peaks consistent with this compound as well.

Neutron diffraction experiments were carried out at the NRC Chalk River laboratory (NRU reactor). There, six crystals were sealed in airtight cans under dry helium, aligned, and inserted into the E3 spectrometer. The (0 0 6) and (1 1 0) rocking curve widths were ∼1° for each crystal, and ∼2.2° for the mosaic of six. Figure 3 shows ortho-II ordering superlattice diffractions via radial scans through $(\frac{3}{2}a^*\ 0\ 0)$ and $(0\ \frac{3}{2}a^*\ 0)$. The detwinning was incomplete – the majority domain occupied only 70% of the sample volume. The neutron study also found that the concentration of Y_2BaCuO_5 in the mosaic was ∼5% by volume, while all other impurity phases constituted less than 1%.

A determination of the oxygen ordering correlation length was resolution limited (horizontal bar in figure 3), but a fit to a resolution-convolved Lorentzian indicated a length >100 Å in the a- and b-directions and ∼50 Å in the c-direction. Given the growth method used, these compare remarkably well with the values of $\xi_a = 148$ Å, $\xi_b = 430$ Å and $\xi_c = 58$ Å obtained in high-purity single crystals[13]. Indeed, they even exceed the correlation lengths found in many flux-grown single crystals.

Further neutron scattering results will be published elsewhere[15].

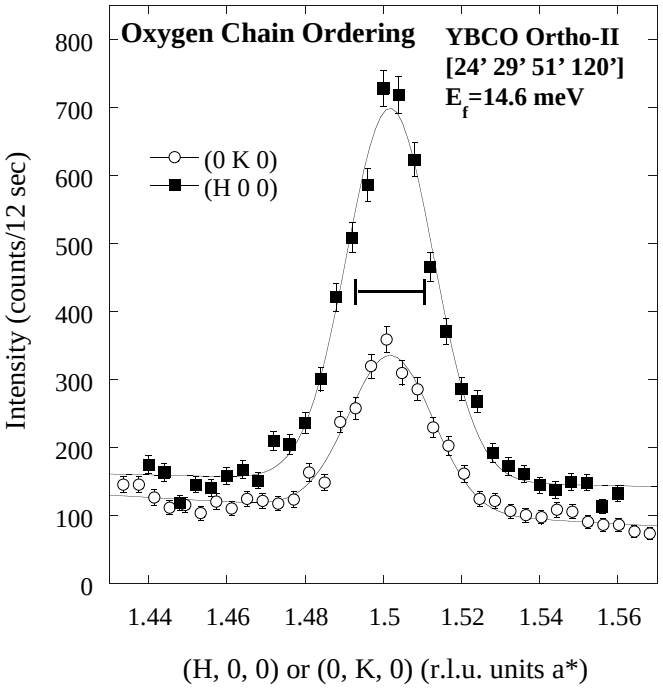

FIG. 3: Radial elastic neutron scattering scans through $(\frac{3}{2}a^*\ 0\ 0)$ and $(0\ \frac{3}{2}a^*\ 0)$, with the experimental resolution indicated. The larger and smaller peaks are from the majority and minority domains, the larger domain accounting for 70% of the sample volume.

4. CONCLUSION

We have grown and detwinned cubic centimetre-size crystals of ortho-II $YBa_2Cu_3O_{6.5}$, with oxygen ordering correlation lengths >100 Å in the plane and ∼50 Å in the c-direction. They contain 5% Y_2BaCuO_5 by volume and are partially detwinned, with 70% of their volume in the major orientation. Each crystal has a rocking curve width of ∼1°. These crystals are currently being studied in detail by neutron scattering, and have already shown that their symmetry is not broken by satellite Bragg peaks associated with static long-range d-density wave order, as is seen in less-ordered crystals[15].

Acknowledgments

This research was supported by the Canadian Institute for Advanced Research. The work at the University of British Columbia and at the University of Toronto was supported by NSERC.

[1] A. Erb, E. Walker, and R. Flükiger, Physica C **245**, 245 (1995).
[2] R. Liang, D. A. Bonn, and W. N. Hardy, Physica C **304**, 105 (1998).
[3] T. Izumi, Y. Nakamura, and Y. Shiohara, J. Mater. Res. **7**, 1621 (1992).
[4] M. Cima, M. C. Fleming, A. M. Figueredo, M. Nakade, H. Ishii, H. D. Brody, and J. S. Haggerty, J. Appl. Phys. **72**, 179 (1992).
[5] C. A. Bateman, L. Zhang, H. M. Chan, and M. P. Harmer, J. Am. Ceram. Soc. **75**, 1281 (1992).
[6] T. Izumi, Y. Nakamura, and Y. Shiohara, J. Cryst. Growth **128**, 757 (1993).
[7] S. Marinel, J. Wang, I. Monot, M. P. Delamare, J. Provost, and G. Desgardin, Supercond. Sci. Tech. **10**, 147 (1997).
[8] D. Shi, K. Lahiri, D. Qu, and S. Sagar, J. Mater. Res. **12**, 3036 (1997).
[9] M. Boffa, M. Boutet, A. D. Trolio, S. Pace, N. Sparvieri, A. M. Testa, and A. Vecchione, Physica C **282**, 487 (1997).
[10] R. Yu, J. Mora, N. Vilalta, F. Sandiumenge, V. Gomis, S. Piñol, and X. Obradors, Supercon. Sci. Tech. **10**, 583 (1997).
[11] Y. Imagawa and Y. Shiohara, Physica C **262**, 243 (1996).
[12] N. Ogawa, I. Hirabayashi, and S. Tanaka, Physica C **177**, 101 (1991).
[13] R. Liang, D. A. Bonn, and W. N. Hardy, Physica C **236**, 57 (2000).
[14] P. Manca, S. Sanna, G. Calestani, A. Migliori, S. Lapinskas, and E. E. Tornau, Phys. Rev. B **63**, 134512 (2001).
[15] C. Stock, W. J. L. Buyers, Z. Tun, R. Liang, D. Peets, D. Bonn, W. N. Hardy, and L. Taillefer, Phys. Rev. B **66**, 024505 (2002), cond-mat/0203076.